Comparative potential of black tea leaves waste to granular activated carbon in adsorption of endocrine disrupting compounds from aqueous solution

Ifelebuegu, A.O.; Ukpebor, J.E.; Obidiegwu, C.C.; Kwofi, B.C.,

ISSN: 2383-3866

Ifelebuegu, A, Ukpebor, J, Obidiegwu, CC & Kwofi, BC 2015, 'Comparative potential of black tea leaves waste to granular activated carbon in adsorption of endocrine disrupting compounds from aqueous solution' *Global Journal of Environmental Science and Management*, vol 1, no. 3, pp. 205-214.http://dx.doi.org/10.1007/s10943-014-9975-3

Published by Global Journal of Environmental Science and Management Available from http://www.gjesm.net/article_12396_0.html

Global J. Environ. Sci. Manage., 1(3): 205-214, Summer 2015
ISSN 2383 - 3572

Comparative potential of black tea leaves waste to granular activated carbon in adsorption of endocrine disrupting compounds from aqueous solution

[1]A.O. Ifelebuegu; [2]J.E. Ukpebor; [1]C.C. Obidiegwu; [1]B.C. Kwofi

[1]Department of Geography, Environment and Society, Coventry University, Coventry CV1 5FB, UK
[2]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ UK

Received 5 March 2015; revised 16 April 2015; accepted 18 April 2015; available online 1 June 2015

ABSTRACT: The adsorption properties and mechanics of selected endocrine disrupting compounds; 17 β-estradiol, 17 α – ethinylestradiol and bisphenol A on locally available black tea leaves waste and granular activated carbon were investigated. The results obtained indicated that the kinetics of adsorption were pH, adsorbent dose, contact time and temperature dependent with equilibrium being reached at 20 to 40 minutes for tea leaves waste and 40 to 60 minutes for granular activated compound. Maximum adsorption capacities of 3.46, 2.44 and 18.35 mg/g were achieved for tea leaves waste compared to granular activated compound capacities of 4.01, 2.97 and 16.26 mg/g for 17 β- estradiol, 17 α-ethinylestradiol and bisphenol A respectively. Tea leaves waste adsorption followed pseudo-first order kinetics while granular activated compound fitted better to the pseudo-second order kinetic model. The experimental isotherm data for both tea leaves waste and granular activated compound showed a good fit to the Langmuir, Freundlich and Temkin isotherm models with the Langmuir model showing the best fit. The thermodynamic and kinetic data for the adsorption indicated that the adsorption process for tea leaves waste was predominantly by physical adsorption while the granular activated compound adsorption was more chemical in nature. The results have demonstrated the potential of waste tea leaves for the adsorptive removal of endocrine disrupting compounds from water.

Keywords: *Adsorption isotherms, Bisphenol A (BPA), Endocrine disrupting compounds (EDCs), Granular activated compound (GAC), Kinetics, Tea leaves waste (TL_H), Thermodynamics, 17 α-ethinylestradiol (EE2), 17 α- estradiol (E2)*

INTRODUCTION

Endocrine Disrupting Compounds (EDCs) are among the pollutants of great concern that have been detected in surface waters, wastewater, run-off and landfill leachates in recent times (Koplin *et al*., 2002; Bennotti *et al*., 2008; Yoon *et al.*, 2010; Ifelebuegu, 2011). EDCs are predominantly discharged into the environment via domestic and industrial wastewater treatment plants before reaching the receiving bodies (Gultekin and Ince, 2007; Liu *et al.*, 2009b). Among the EDCs, 17 β- estradiol (E2), 17 α-ethinylestradiol (EE2) and bisphenol A (BPA) are frequently detected in wastewater around the globe. E2 is a natural occurring steroid hormone excreted by humans. EE2 is mainly used as an oral contraceptive (Sun *et al*., 2010). BPA is mainly used in the plastic industry as a monomer for the production of polycarbonate and epoxy resins. These chemicals elicit adverse effects on the endocrine systems in humans and wildlife leading to developmental defects and inhibition of embryos (Helland, 2006; Koh *et al.*, 2008; Chang *et al.*, 2009a, 2009b; Cases *et al.*, 2011). Human exposure to these EDCs in the environment are of great concern because of their potential long term impacts on humans (Liu *et al.*, 2009a).

The adsorption process is a widely studied and utilised in the removal of EDCs from aqueous solutions by use of adsorbent materials such as activated

*Corresponding Author Email: *A.Ifelebuegu@coventry.ac.uk*
Tel.: +442476887690; Fax: +442476887690

Note. This manuscript was submitted on March 5, 2015; approved on April 18, 2015; published online on June 1, 2015. Discussion period open until October 1, 2015; discussion can be performed online on the Website "Show article" section for this article. This paper is part of the Global Journal of Environmental Science and Management (GJESM).

carbon. The removal process often involve hydrophobic interaction (Koh *et al.,* 2008). The use of Granular activated carbon (GAC) adsorption for the removal of both synthetic and naturally occurring organic pollutants from water and wastewater has been extensively studied (Zhang and Zhou, 2008). They have been proven to be effective for the removal of EDCs (Zhang and Zhou, 2005; Ifelebuegu *et al.*, 2006; Ifelebuegu, 2012). However, the relatively high cost of GAC has prevented its more widely used application especially in developing countries for the effective removal of EDCs in water and wastewater. There is therefore a growing need for cheaper, reliable, effective and environmental friendly alternatives for the removal of organic contaminants in water and wastewater (Park *et al.,* 2014). The use of spent black tea leaves (TL_H) is one of such alternative that is not only cheap and readily available but also environmentally relevant as it recycles waste products. With an annual black tea leaves consumption of more than 2 million tonnes globally, the use of TL_H could be an effective and environmentally friendly alternative to the more expensive activated carbon. The current work compares the removal efficiency of TL_H to that of the GAC for the removal of E2, EE2 and BPA (chemical structures are represented in Fig. 1) from aqueous solution.

MATERIALS AND METHODS

Materials

Analytical grade methanol, sodium hydroxide (NaOH) and ortho-phosphoric acid were purchased from Fisher Scientific (UK), E2; EE2 and BPA standards were obtained from Sigma-Aldrich (UK). The GAC (20-40 mesh), was purchased from Jacobi Carbon (Merseyside, UK). The GAC has been previously characterised (Ifelebuegu, 2012). Deionised water (DI) was used for all sample preparation unless otherwise stated. A readily available box of black tea (~750 g) was obtained from a local supermarket. Stock solutions (~1 g/L) of E2, EE2 and BPA, were prepared in 100% methanol and serial dilution carried out to attain the calibration curve. The standards were stored in the fridge <4°C until needed. Analysis was done using external calibration with a concentration range of 0.5 – 2 mg/L.

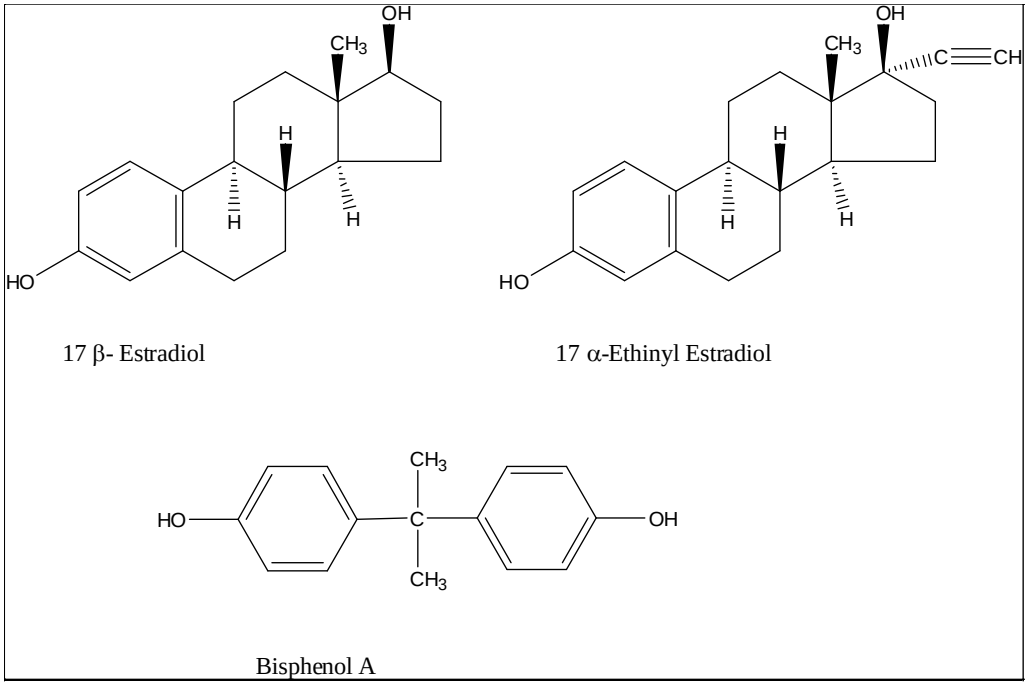

Fig. 1: Chemical structure of the test chemicals: 17 b-estradiol [(E2), mol. wt. = 272.3 g/mol], 17 α-ethinyl-estradiol [(EE2), mol. wt. = 296.2 g/mol] and Bisphenol A [(BPA), mol. wt. = 228.1 g/mol]

Tea Adsorbent Preparation

Tea bags were prepared for the experiments using a method developed by Yoshita *et al.,* (2009). The tea bags were drenched and washed severally in hot water (about 80-100°C) to remove colouring compounds and turbidity. They were washed continuously with deionised water until a clear solution was obtained. The tea samples (TL_H) were then dried in an oven at -80°C for 24 hours. The leaves were finally pulverized, passed through a 600 µm sieve and stored in clean air tight bottles.

Batch Adsorption Experiments

0.1 g, 0.2 g, 0.4 g, 0.8 g, and 1 g of the different adsorbents were weighed into different labelled 250 mL conical flasks. 200 mL of 2 mg/l solutions of E2, EE2, and BPA was then transferred into conical flasks. The flasks were then shaken at a speed of 7 rpm. Aliquots of the samples were collected at different time intervals (0 to 60 mins) and filtered using a Whatman filter paper. The absorbent coefficient was determined using equation 1:

$$q_e\,(mg/g) = \frac{C_0 - C_e\,(mg/L)}{m\,(g)} \times V\,(mL) \quad (1)$$

where: q_e = adsorption equilibrium in mg/g
C_o and C_e = initial and equilibrium concentration respectively (mg/L)
m = mass of adsorbent (g)
V = volume of aqueous solution (mL)
The adsorption efficiency for the different compounds was also calculated using the equation 2:

$$\text{Percent removal}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

Where C_o = initial concentration (mg/L)
C_e = concentration at equilibrium (mg/L)

Effects of pH

The effects of pH on the adsorption of E2, EE2, and BPA using TL_H were investigated in batch adsorption experiments at varying pHs of 3, 5, 7, 8 and 9, with other variables kept constant at 2 mg/l concentrations of E2, EE2 and BPA, in 200 mL volumetric flasks, temperature of 25 °C ± 2 °C and 0.4 g adsorbent dose of TL_H. The pH values were adjusted with 0.1 N NaOH and concentrated HCl solutions and measured using a pH meter. Samples were agitated at a constant speed of 200 rpm and aliquots withdrawn for analysis after 60 minutes of agitation (Zhang and Zhou, 2005).

Adsorption Kinetics and Thermodynamics

The initial experiments on the effect of adsorbent dose on adsorption, found 0.4g as the optimum dose per unit gram of the adsorbates. This weight was maintained in carrying out the investigations on the kinetic and thermodynamic of adsorption of E2, EE2 and BPA onto TL_H and GAC. 0.4g of TL_H and GAC adsorbents were weighed into 250 mL conical flasks and prepared solutions of E2, EE2, and BPA at 2 mg/L concentration added. The samples were agitated at a speed of 200 rpm under different controlled temperatures of 15°C, 20°C, 25°C, 30°C ±0.2. Aliquots of the treated water were withdrawn at intervals ranging from 0 min to 60 min for analysis. Experimental data was analysed using the Langmuir, Freundlich and Temkin models as have been previously described (Ifelebuegu, 2012; Ghaedi *et al.,* 2014).

Analytical Methods

Samples were analyzed using a high-performance liquid chromatography (HPLC) fitted with a fluorescence detector. The HPLC system (Hewlett Packard series 1050) consisted of Quaternary pump (model 79852A -United Kingdom), a 21 vial autosampler (model 79855A, Germany) and the data were analysed using Agilent ChemStation® software. Chromatographic separation was achieved using a C18 ODS-Hypersil analytical column (150 x 4.6mm, 5µm) maintained at 30^0C temperature. Details of the analytical procedures have been previously described by Ifelebuegu *et al*., (2010).

RESULTS AND DISCUSSION

Effect of pH

pH has been known to influence the surface charges on different adsorbent materials, as well as the ionisation of chemicals (Zhang and Zhou, 2005). The adsorbent efficiency was studied at pHs 3, 5, 7, 8 and 9, covering acidic, neutral and basic medium conditions. Percentage removal using TL_H was found to be higher in the acidic and neutral pH ranges, but was found to decrease with an increase in pH (Fig. 2). Huang *et al.,* (2007) also found pH to play a significant role in the process of adsorption. E2, EE2 and BPA adsorption was found to be significantly lower at

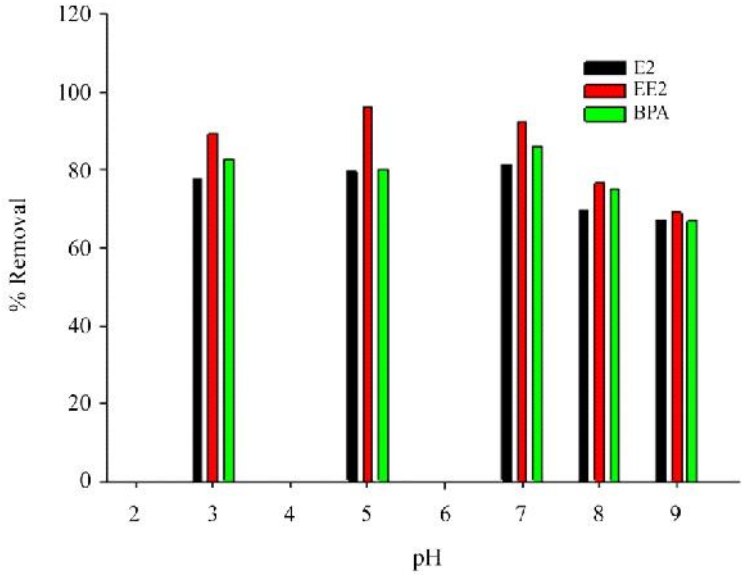

Fig. 2: Effect of pH on adsorption

higher pH (pH > 8) than at lower pH. Similar trends were observed by Kouras *et al.*, (1995) and Zhang and Zhou, (2005) using powdered activated carbon. This trend could be due to the electrostatic repulsion which exist between the adsorbate molecules and the surface of the adsorbent, as the pH increased. (Cuerda-Correa *et al.*, 2010; Ifelebuegu, 2012). The effects of pH on the adsorption by the GAC used in this research has been previously reported (Ifelebuegu, 2012) and a similar trend was observed with the highest adsorption at the neutral to slightly acidic pHs.

Effect of Adsorbent Dose and Contact Time

The rate of adsorption was found to increase with increase in the dose of the adsorbents from 0.1 g to 1.0 g in the nominal concentration of 2 mg/L for each of the test chemicals. The increase is likely as a result of the availability of more sorption sites for adsorption as have been previously reported (Yoon *et al.*, 2003; Cardoso *et al.*, 2011). Also, the increase was found to be gradual until equilibrium was attained. The highest dose of 1 g GAC was able to achieve removal of 96.98% for E2, 97.05% for EE2 and 96.21% for BPA while TL_H attained removal of 95.75%, 95.25% and 96.19% for E2, EE2 and BPA respectively (Fig. 3). It can also be seen that TL_H attained relative equilibrium within 20 to 40 minutes for all the adsorbates. Comparatively, GAC took more time to attain equilibrium, with all three adsorbates reaching equilibrium at 40 to 60 minutes.

Adsorption Kinetic and Isotherm

Pseudo First and Second Order Kinetics

In this study, the mechanism of adsorption was investigated by using various kinetic models based on aqueous phase concentrations of the adsorbates. Pseudo-first and second-order models as proposed by Lagergren, (1898) were used in the investigation, which are expressed as:

$$\frac{dq}{dt} = k_1(qe - q) \quad (3)$$

$$\frac{dq}{dt} = k_2(qe - q)^2 \quad (4)$$

Where t is the contact time (min), k_1 = pseudo-first-order adsorption rate constant (1/min), q_e and q are the amount of the adsorbate at equilibrium and time t (mg/g) respectively. Equations 3 and 4 can be expressed in an integral form as equations 5 and 6 respectively.

$$\ln C/C_0 = -kt \quad (5)$$

$$\frac{1}{[C]} - \frac{1}{[C_0]} = kt \quad (6)$$

Pseudo first order plot of In C/C_0 against t should give a linear relationship from which k_1 in (1/min) can

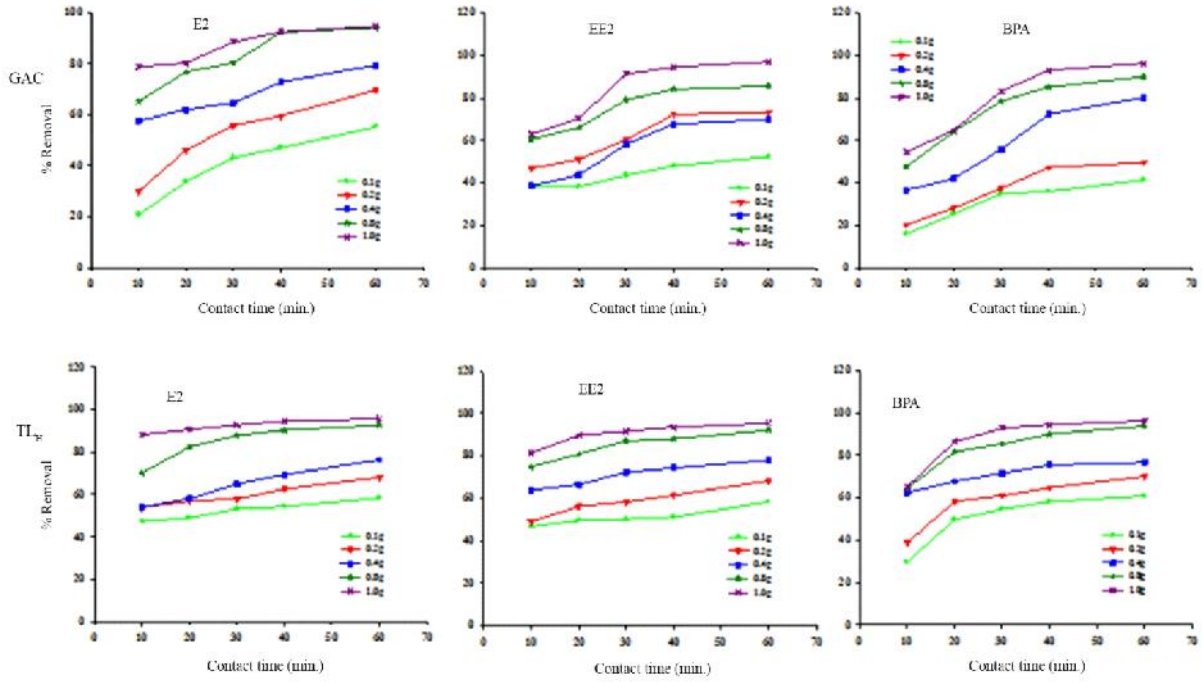

Fig. 3: Effect of adsorbent dose (GAC and TL_H) and contact time on the removal efficiency of E2, EE2 and BPA at pH 5

be calculated from the slope obtained from the graph. A plot of $1/[C] - 1/[C_o]$ against t will give a rate constant K_2 (L/mg/min) for pseudo-second-order adsorption kinetics. Tables 1 and 2 depicts the results obtained for the pseudo first-order and pseudo second-order kinetic models for TL_H and GAC respectively.

The rate constant for the adsorption of E2 was found to be highest in TL_H with values of 0.0137 1/min, then followed by EE2 0.0102 1/min and finally 0.0097 1/min for BPA (Table 1). It was found to follow the trend E2> EE2> BPA. However, for GAC (Table 2), a reverse trend (BPA>EE2>E2) was observed with BPA having the highest rate constant (0.0253 1/min) and E2 with the lowest 0.0149 1/min.

The adsorption of E2 EE2 and BPA onto TL_H was better described by the pseudo first order kinetics, indicating a predominantly physical adsorption mechanism, while the adsorption onto GAC showed a superior fit to pseudo-second-order kinetics which suggests that chemisorption is the rate determining step for adsorption onto GAC. (Ho and McKay, 1998; Ifelebuegu, 2012).

Adsorption Isotherms Studies

Adsorption isotherms are usually employed to better understand the adsorption process for the studied adsorbates. This helps in modelling design parameters in full scale applications (Ifelebuegu *et al.*, 2015) The equilibrium data obtained for E2, EE2 and BPA for their adsorption onto TL_H and GAC was analysed using the Langmuir, Freundlich and Temkin adsorption isotherm models.

The linear form of the Langmuir isotherm is expressed in equation 7 as:

$$\frac{1}{X/M} = \frac{1}{b} + \frac{1}{ab} \times \frac{1}{C_e} \quad (7)$$

where:

X – the mass of adsorbate (mg)

M – the mass of adsorbent (mg)

C_e – the concentration of solute remaining at equilibrium in mg/L

a, b – the constants. a is coefficient, and b is the amount of adsorbate needed to form a complete monolayer on the adsorbent surface and so increases

Table 1: Pseudo first and second order kinetics for TL_H

Adsorbate	Pseudo first order			Second order		
	Line equation	K_1(1/min)	R^2	Line equation	K_2(L/mg/min)	R^2
E2	y = -0.0137x – 0.6265	0.0137	0.995	y = 0.0211x + 0.3161	0.0211	0.988
EE2	y = -0.0102x – 0.9245	0.0102	0.967	y = 0.0187x + 05949	0.0187	0.856
BPA	y = -0.0097x - 09349	0.0097	0.987	y = 0.0168x + 0.7256	0.0168	0.928

Table 2: Pseudo first and second order kinetics for GAC

Adsorbate	Pseudo first order			Second order		
	Line equation	K_1(1/min)	R^2	Line equation	K_2(L/mg/min)	R^2
E2	y = -0.0149x – 0.6729	0.0149	0.974	y = 0.0258x + 0.3112	0.0258	0.983
EE2	y = -0.0157x – 0.3481	0.0157	0.897	y = 0.0188x + 0.1167	0.0188	0.974
BPA	y = -0.0253x – 0.1332	0.0253	0.959	y = 0.0372x + 0.2704	0.0372	0.951

with molecular size. A plot of (1/(X/M)) against ($1/C_e$) gave a straight line.

The linearised form of the Freundlich isotherm is expressed in equation 8:

$$\log X/M = \log k_f + 1/n \log C_e \quad (8)$$

where:

X = the mass of adsorbate (mg)

M = the mass of adsorbent (mg)

C_e = the concentration of solute remaining at equilibrium in mg/L

K_f and n – constants derived from the adsorption isotherm by plotting (X/M) against C_e on log-log paper which produces a straight line with a slope 1/n while the y-intercept is K_f.

The Temkin isotherm model is one which presumes that as a result of sorbate-sorbate interactions, the temperature of all molecules in a layer declines linearly with coverage. The sorption is also described by consistent distribution of binding energies (Shah *et al.*, 2012)

The linearised form of the Temkin isotherm is expressed in equation 9 and 10 as:

$$q_e = B \ln A_T + B \ln Ce \quad (9)$$

$$\text{with } B = RT/b_T \quad (10)$$

Where:

A_T = Temkin isotherm equilibrium binding constant (L/mg)

b_T = Temkin isotherm constant

R = Universal gas constant (8.314 J/mol/K)

B = Constant related to heat of adsorption (J/mol).

The Langmuir, Freundlich and Temkin coefficients for single solute adsorption isotherms and their corresponding correlation coefficients are presented in Table 3. The fitting of the adsorption isotherm data for E2 EE2 and BPA showed relatively good fit to all three isotherm model with the Langmuir isotherm being superior based on the highest correlation coefficients. From Table 3 it can be seen that TL_H had a comparative adsorption capacity to GAC for E2, EE2 and BPA.

The Freundlich isotherm is an empirical equation that assumes the adsorption processes take place on heterogeneous surfaces and adsorption capacity is related to the concentration of the test chemical (E2, EE2 and BPA) at equilibrium. K_F (mg/g) and n provide an indication of the adsorption capacity and the adsorption intensity respectively (Hameed, 2009). The magnitude of the exponent 1/n gives an indication of the favourability of adsorption with values of n>1 represents favourable adsorption conditions (Treybal, 1968; Ho and McKay, 1998). With n values greater than unity for all adsorbate, it demonstrates that the EDCs are all favourably adsorbed onto TL_H, similar to GAC. The mechanism for most EDCs on all adsorbents is believed to be of a different nature, which may involve non – specific molecular interactions between adsorbent and adsorbate with focused explanation on physical adsorption, hydrogen bonding and coordination complexes (Saha *et al.*, 2010).

Effect of Temperature and Adsorption Thermodynamics

Temperature was also found to play a significant role in the adsorption thermodynamics of the two adsorbent studied. The temperature effects were

Table 3: Langmuir and Freundlich, Temkin isotherm parameters for TL_H and GAC at 298K

Compound	Langmuir			Freundlich			Temkin		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f	1/n	R^2	A (L/mg)	B	R^2
				TL_H					
E2	3.4610	0.1490	0.9960	1.7640	0.3760	0.9500	1.7180	3.5350	0.9490
EE2	2.4420	0.1880	0.9930	3.7740	0.4780	0.9690	1.6700	3.0870	0.9780
BPA	18.3250	0.0390	0.9990	15.4240	0.1310	0.9440	1.9970	9.5260	0.9490
				GAC					
E2	4.0126	0.2000	0.9770	4.2510	0.4860	0.9560	1.8590	3.3920	0.9830
EE2	2.9740	0.2480	0.9760	3.6120	0.5540	0.9640	1.6970	3.0290	0.9870
BPA	16.2610	0.0930	0.9790	10.5490	0.2710	0.9250	1.9670	5.0650	0.9600

studied at 15, 20, 25 and 30°C. Sorption of two of the test chemicals (E2 and EE2) exhibited an increase with temperature (Fig. 4). This could be as a result of decreased solution viscosity hence, a higher mass transfer and diffusion rates of E2 and EE2 molecules.

Fig. 4 also showed that BPA showed increased adsorption at lower temperatures. This decreased adsorption capacity with increasing temperature for BPA was also observed by Liu *et al.,* (2009a) when investigating BPA adsorption onto various forms of activated carbon. Similarly, Park *et al.,* (2014) when studying BPA adsorption onto organo-clay, observed that the value of the free energy became more negative with a decrease in temperature indicating that BPA adsorption was more favourable at lower temperatures. To better understand the adsorptive properties and temperature effects, the thermodynamic parameters (Gibb's free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0)) were evaluated from equations 11 to 13:

$$(\Delta G^0) = - RT\ln K_D \quad (11)$$

$$(\Delta G^0) = (\Delta H^0) - T(\Delta S^0) \quad (12)$$

$$RT\ln K_D = (\Delta H^0) - T(\Delta S^0) \quad (13)$$

Where R is universal gas constant, T is the temperature in Kelvin (^{0}K) and $k_D = (q_e / C_e)$ = quantity of adsorbate that adsorbed onto the adsorbent l/g. The plot of ln k_D vs 1/T gave a straight line with ΔH^0 and ΔS^0 values obtained from the slope and intercept of the graph respectively. The thermodynamic parameters obtained from the graph are shown in Table 4. The negative values of ΔG^o at – 27.68, - 24.03 and -10.11 for E2, EE2 and BPA respectively for TL_H and -10.94 (E2), -11.83 (EE2) and -3.58 for GAC indicates the feasibility and spontaneity of the adsorption process for both adsorbents. The negative values of ΔG^o compare favourably with the values reported by Turku *et al.,* (2009) for the adsorption of E2 onto polymeric adsorbents and GAC. The enthalpy of reaction for the adsorption of E2, EE2 and BPA onto TL_H and BPA onto GAC are all negative indicating the physical nature of the adsorption process. Positive enthalpy values of 91 and 95 KJ/mol were obtained for E2 and EE2 respectively, for their adsorption onto GAC. Positive values are not common, but similar positive values have been reported previously by Turku *et al.,* (2009); Liu *et al.,* (2009a) and Ifelebuegu, (2012). Also Al-Degs *et al.,* (2008) reported similar positive values for the adsorption of dyes unto GAC. A positive enthalpy values indicate a feasible but non spontaneous endothermic reaction with predominantly chemical interaction between the adsorbate and adsorbent. A positive entropy change for both TL_H and GAC (93 to 339 J/mol and 2 to 37 J/mol, respectively) suggests an increased randomness at the solid/ solution interface. This also corresponds to an increase in the degree of freedom of the adsorbed species.

CONCLUSION

Waste tea leaves were effective in the adsorption of E2, EE2 and BPA from aqueous solutions and showed comparable adsorption capacity to GAC. Adsorption capacity was highest at acidic to neutral pH with equilibrium being reached at within 20 to 40 minutes for TL_H. Maximum adsorption capacities for E2, EE2 and BPA, were 3.46, 2.44, 18.35 mg/g for TL_H and 4.01, 2.97 and 16.26 mg/g for GAC respectively. The negative values of "G° at – 27.68, - 24.03 and - 10.11 for E2, EE2

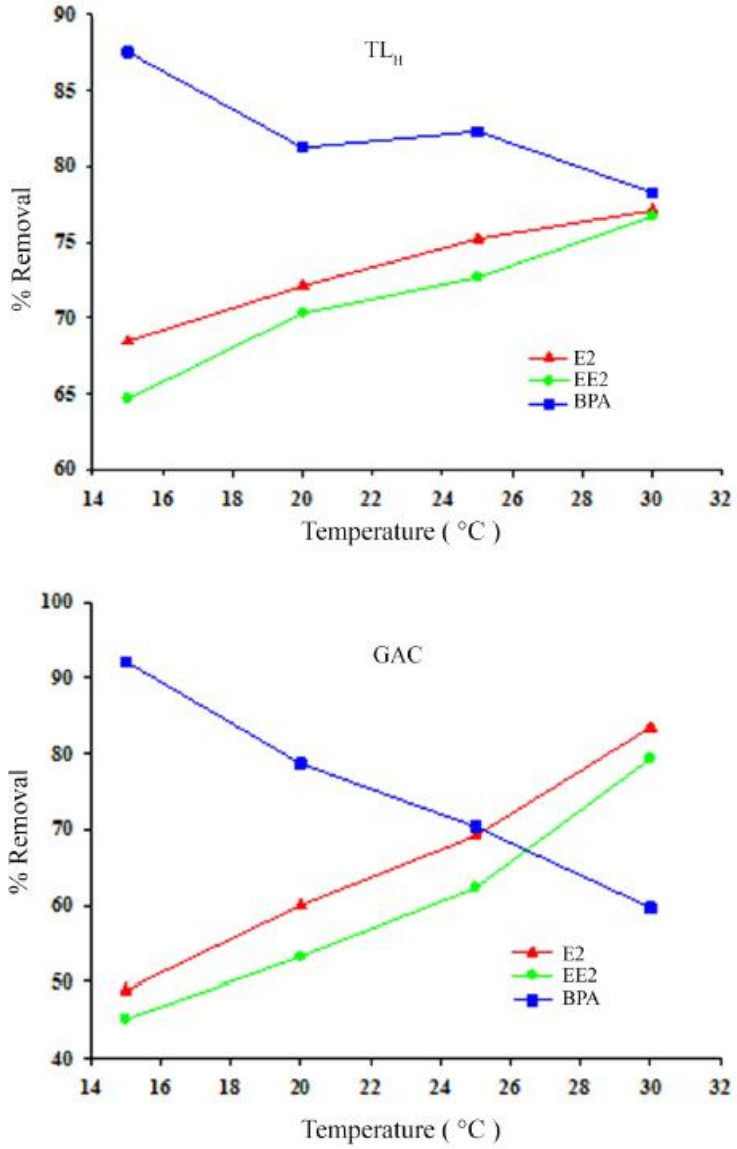

Fig. 4: Effect of temperature on the adsorption and percentage removal of E2, EE2 and BPA on GAC and TL_H adsorbent at pH 7

Table 4: Enthalpy, entropy and gibbs free energy for TL_H and GAC at 298K

	TL_H			GAC		
	Gibbs free energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/mol)	Gibbs free energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/mol)
E2	-27.68 ± 1.8	-22.70± 5	92.81± 4.5	-10.94± 1.5	91.00 ± 5.1	37.00 ±6.2
EE2	-24.03 ± 2.8	-19.21± 5	86.56 ± 3.8	-11.83± 2.4	95.00 ± 4.5	40.00 ± 4.3
BPA	-10.11 ± 0.5	-99.80± 5	338.9 ± 22.6	-3.58± 0.5	-8.04 ± 1.5	11.99± 2.0

and BPA respectively for TL_H and -10.94 (E2), -11.83 (EE2) and -3.58 for GAC indicated the feasibility and spontaneity of the adsorption process for both adsorbents. The enthalpy of reaction for the adsorption of E2, EE2 and BPA onto TL_H and BPA onto GAC are all negative indicating the physical nature of the adsorption process. While the positive value of 91 and 95 KJ/mol for E2 and EE2 respectively for their adsorption onto GAC indicate a feasible but non-spontaneous endothermic reaction with predominantly chemical interaction between the adsorbate and adsorbent. A positive entropy change for both TL_H and GAC (92.81 to 338.9 J/mol for TL_H and 1.99 to 37 J/mol) suggests an increased randomness at the solid/solution interface. This also corresponds to an increase in the degree of freedom of the adsorbed species. The adsorption equilibrium data for both TL_H and GAC were fitted to the Langmuir, Freundlich and Temkin isotherm models and the Langmuir isotherm model showed the best fit for all the adsorbates. Waste tea leaves can, therefore, be used as an economic alternative to GAC for the adsorptive removal of EDCs from water and wastewater.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

Bennotti, M. J.; Trenholm, R. A.; Vanderford, B. J.; Holady, J. C.; Stanford B. D. Snyder, S. A., (2008). Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water, Environ. Sci. Tech., (43): 597-603 **(7 pages)**.

Cases, V.; Alonso, V.; Argandona, V.; Rodriguez, M.; Prats, D., (2011). Endocrine disrupting compounds: A comparison of removal between conventional activated sludge and membrane bioreactors, Desalination, 272(1-3): 240-245 **(6 pages).**

Chang, E.E.; Chen, Y.; Lin Y.; Chiang P., (2009a). Reduction of natural organic matter by nanofiltration process, Chemosphere, (76): 1265-1272 **(8 pages)**.

Chang, H.; Choo, K.; Lee B.; Choi, S., (2009b). The method of identification, analysis and removal of endocrine disrupting compounds (EDCs) in water, J. Hazard. Mater., (172): 1-12 **(12 pages)**.

Cardoso, N.F.; Lima, E.C.; Pinto, I. S.; Amavisca, C.V.; Royer, B.; Pinto, R. B.; Pereira, S. F., (2011). Application of cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution, J. Environ. Manag., 92(4): 1237-1247 **(11 pages)**.

Cuerda-Correa, EM.; Domínguez-Vargas, J.R.; Olivares-Marín, F.J.; de Heredia, J.B., (2010). On the use of carbon blacks as potential low-cost adsorbents for the removal of non-steroidal anti-inflammatory drugs from river water, J. Hazard. Mater., 177 (1): 1046-1053 **(8 pages).**

Ghaedi, M.; Ghaedi, A.M.; Negintaji, E.; Ansari, A.; Vafaei, A.; Rajabi, M., (2014). Random forest models for the removal of bromophenol blue using activated carbon obtained from Astragalus Bisulcatus tree, J. Ind. Eng. Chem., (20): 1793 - 1803 **(11 pages)**.

Gultekin, I.; Ince, N.H., (2007). Synthetic endocrine disruptors in the environment and water remediation by advanced oxidation processes, J. Environ. Manag., 85(4): 816-832 **(17 pages)**.

Hameed, B.H., (2009). A new non - conventional and low - cost adsorbent for removal of basic dye from aqueous solutions, J. Hazard. Mater., 161(2-3): 753-759 **(7 pages)**.

Helland, J., (2006). Endocrine disrupters as emerging contaminants in wastewater. Minnosota House of Representatives.

Ho, Y. S.; McKay, G., (1998). Sorption of dye from aqueous solution by peat, Chem. Eng. J., (70): 115-124 **(10 pages)**.

Huang, X.; Gao, N.; Zhang, Q., (2007). Thermodynamics and kinetics of cadmium adsorption unto oxidized granulated activated carbon, J. Environ. Sci., (19): 1287-1292 **(5 pages)**.

Ifelebuegu, A.O.; Lester, J.N.; Churchley, J.; Cartmell, E., (2006). Removal of an endocrine disrupting chemical (17alpha-ethinyloestradiol) from wastewater effluent by activated carbon adsorption: effects of activated carbon type and competitive adsorption, Environ. Tech., (27): 1343-1349 **(7 pages)**.

Ifelebuegu, A.O.; Theophilus, S.C.; Bateman, M.J., (2010). Mechanistic evaluation of the sorption properties of endocrine disrupting chemicals in sewage sludge, Int. J. Environ. Sci. Tech., 7(4): 617-622 **(6 pages)**.

Ifelebuegu, A.O., (2011). The fate and behaviour of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes, Int. J. Environ. Sci. Tech., 8(2): 245-254 **(10 pages)**.

Ifelebuegu, A.O., (2012). Removal of steroid hormones by activated carbon adsorption kinetic and thermodynamic studies, J. Environ. Protect., 3(6): 469 - 475 **(7 pages)**.

Ifelebuegu, A.O.; Nguyen, T.V.A.; Ukotije-Ikwut, P.; Momoh, Z., (2015). Liquid-phase sorption characteristics of human hair as a natural oil spill sorbent, J. Eviron. Chem. Eng., . doi:10.1016/j.jece.2015.02.015

Koh, Y.K.K.; Chiu, T.Y.; Boobis, A.; Cartmell, E.; Scrimshaw. M.D.; Lester, J.N., (2008). Treatment and removal strategies for estrogen from wastewater, Environ. Technol., (29): 245-267 **(33 pages)**.

Koplin, D.W.; Furlong, E.T.; Meyer, M.T.; Thurman, E. M.; Zaugg, S.D.; Barber, L.B.; Buxton, H.T., (2002). Pharmaceuticals, hormones and other organic wastewater contaminants in US streams 1999-2000: a national reconnaissance, Sci. Total Environ., (36): 1202-1211 **(10 pages)**.

Kouras, A.; Zouboulis, A.; Samara, C.; Kouimtzia, T., (1995). Removal of pesticide from surface water by combined physico - chemical process, Chemosphere, (30): 2307-2315 **(9 pages)**.

Liu, G.; Ma, J.; Li, X.; Qin, Q., (2009a). Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments, J. Hazard. Mater., 164 (2): 1275-1280 **(6 pages).**

Liu, Z.H.; Kanjo, Y.; Mizutani, S., (2009b). Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment - physical means, biodegradation and chemical advanced oxidation: A review, Sci. Total Environ., 407(1): 731-748 **(18 pages)**.

Park, Y.; Sun, Z.; Ayoko, G.A.; Frost, R.L., (2014). Bisphenol A sorption by organo-montmorillonite: Implications for

the removal of organic contaminants from water, Chemosphere, (107): 249-256 **(8 pages)**.

Saha, B.; Karounou, E.; Streat, M., (2010). Removal of 17 b-oestradiol and 17 a-ethinyl oestradiol from water by activated carbons and hypercrosslinked polymeric phases, React. Funct. Polym., 70(8): 531-544 **(14 pages).**

Shah, J.; Jan, M. R.; Haq, A.; Zeeshan, M., (2012). Equilibrium, kinetic and thermodynamic studies for sorption of Ni (ii) from aqueous solution using formaldehyde treated waste tea leave, J. Saudi Chem. Soc., doi:10.1016/ j.jscs.2012.04.004

Sun, K.; Gao, B.; Zhang, Z.; Zhang, G.; Liu, X.; Zhao, Y.; Xing, B., (2010). Sorption of endocrine disrupting chemicals by condensed organic matter in soils and sediments, Chemosphere, (80): 709-715 **(7 pages).**

Treybal, R.E., (1968). Mass transfer operations. New York, McGraw Hill.

Yoon, Y., Ryu, J.; Oh, J.; Choi, B.G.; Snyder, S.A., (2010). Occurrence of endocrine disrupting compounds, pharmaceuticals and personal care products in the Hans River (Seoul, South Korea), Sci. Total Environ., (408): 636-643 **(8 pages).**

Yoon, Y.; Westerhoff, P.; Snyder, S.A., Esparza, M., (2003). HPLC fluorescence detection and adsorption of bisphenol A, 17 b-estradiol and 17 a-ethynyl estradiol on powdered activated carbon, Water Res., 37(14): 3530-3537 **(8 pages).**

Yoshita, A.; Lu, J.L.; Ye, J.H.; Liang, Y.R., (2009). Sorption of lead from aqueous solutions by spent tea leaf, African J. Biotechnol., 8(10): 2212-2217 **(6 pages).**

Zhang, Y.; Zhou, J. L., (2005). Removal of estrone and 17 b-estradiol from water by adsorption, Water Res., 39 (16): 3991-4003 **(13 pages)**.

Zhang, Y.; Zhou, J.L., (2008). Occurrences and removal of endocrine disrupting chemicals in wastewater, Chemosphere, 73 (5): 848-853 **(6 pages)**.

AUTHOR (S) BIOSKETCHES

Ifelebuegu, A.O., Ph.D., Professor; Department of Geography, Environment and Society, Coventry University, Coventry CV1 5FB, UK.
Email: *a.ifelebuegu@coventry.ac.uk*

Ukpebor, J.E., Ph.D., Professor; Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ UK.
Email: *jukpebor@yahoo.com*

Obidiegwu, C.C., MSc Student; Department of Geography, Environment and Society, Coventry University, Coventry CV1 5FB, UK.
Email: *obidiegwuc@uni.coventry.ac.uk*

Kwofi, B.C., MSc Student; Department of Geography, Environment and Society, Coventry University, Coventry CV1 5FB, UK.
Email: *kwofib@uni.coventry.ac.uk*

How to cite this article: (Harvard style)
Ifelebuegu, A.O.; Ukpebor, J.E.; Obidiegwu, C.C.; Kwofi, B.C., (2015). Comparative potential of black tea leaves waste to granular activated carbon in adsorption of endocrine disrupting compounds from aqueous solution, Global J. Environ. Sci. Manage., 1(3): 205-214.